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(54) Title: FUNCTIONAL TREATMENT OF TEXTILE MATERIALS

(57) Abstract: A novel technology was proposed to use the nano-particles with all their three dimensions ranging from 1 to 100 nm, which are coupled on the fiber molecules with covalent bonds, or bound on fiber's surface, to impart numerous functions. The nano-particles are clathrate compounds, dendritic compounds, star compounds, inorganic particles or cross-linked networks. The selected clathrates complex the non-polar molecules or non-polar segments of compound, etc. to form more and stabilize more perfect helix structures. The non-polar molecules are ethylene glycol and its derivatives and polymers, polyolefin, hydrocarbon, polyolefin oxide etc. The non-polar segments of compounds are involved in the compounds, i.e. stearic acid and its esters or salts, organic acids and their esters or salts, anionic, cationic or nonionic surfactants, amines, amides etc.

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Patent Application of  
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for

5           ***TITLE: FUNCTIONAL TREATMENT OF TEXTILE MATERIALS***

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Patent Applications Serial No. 60/283,400, filed April 12, 2001 and Serial No. 60/293,412, filed May 24, 2001, the disclosures  
10 of which are incorporated herein by reference in their entirety.

TECHNICAL FIELD

This invention relates generally to technologies and materials in chemical treatments of  
15 natural and man-made fiber textile materials with the application of nano-technology, to impart properties thereon such as odor-control, soil release, better abrasion resistance, better performance, better hand and adding-weight.

BACKGROUND ART

20           Applying chemical treatments to textile materials, particularly, in fabric and garment forms has been the subject of intensive research for over 70 years. Extensive reviews have been published in this field. A large majority of these published researches are never adopted in industry due to their various drawbacks, such as the cost, the environment problems and  
25 government regulations. Main focus of current work is centered on optimizing existing technology to reduce costs and comply with government regulations. Textile chemists have been dreaming and looking for new technology and material to revolutionize this process for a long time. With the thriving of nano-technology and materials recently, a new era in the chemical treatment of natural and man-made fiber textile materials is coming.

M. S. P. Shaffer etc. [Advanced Materials, April, 30<sup>th</sup>, 1999] used carbon nano-tube to improve the mechanical properties of synthetic fiber. R. A. Vaia etc. [Chem. Mater, 10(8), 2030-2032, 1998] presented a way to impart the property of conductivity to synthetic fiber with metal nano fibril. There are no covalent bonds to couple nano material to fiber molecules in these works. These techniques are not suitable to natural fibers because of the lack of durability.

David S. Soane, [PCT WO 99/49124; 99/49125] claimed to attach functional molecules to material with covalent bond to impart properties of water and oil repellency to textile and other materials. This is not a nano-technology and it does not use nano material at all. Its negative effect on natural fibers' characteristics, such as suitable moisture regain and natural handle should be concerned.

In earlier time, E. A. Beck etc. [USP 3,350,162, 1967] claimed to use amylopectin in finish solution for a water insoluble stiffening finish of fabrics. Authors emphasized that the amylopectin must be branched to possess cool water solubility distinguishing from starch granule and amylose. The molecular weight (MW) of amylopectin is in the range of  $10^7$  -  $10^8$ , which is obviously not in the range of nano size and is difficult to penetrate into the fiber structure. G. M. Richardson etc. [USP 2,661,312, 1953] claimed to introduce the pearl cornstarch in finish solution to stabilize the viscosity of the finish solution at different temperatures. Clearly, such a huge MW starch is difficult to penetrate into fiber structure and to form a nano-helix particle. T. M. Coffindaffer [USP 4,923,623, 1990] claimed to employ pre-ironing spray-liquid to improve wrinkle resistance of fabrics. Such a liquid comprises starch and amine functional silicon compound which can be polymerized to be a film during ironing. The starch was used as a carrier to adjust the viscosity and stabilize the liquid only.

Hodul-P etc. demonstrated to use  $\beta$ -cyclodextrin as an additive to be coupled onto cotton molecules [Vlakna-a-Textil, 1999,6(4),159-161]. It is concluded that after this treatment, this fabric 'does not show negative effect on the whiteness, decreases the loss of tensile strength during curing, causes the lowering of dry wrinkle recovery angles'. No other properties such as odor-control, soil release and better hand were reported. The effect of  $\beta$ -cyclodextrin on the finished products is limited by its low solubility in water, 1.84% only. The size of  $\beta$ -cyclodextrin

is 1.54 nm in diameter, 0.79-0.80 nm in thickness [Kirk Smith, Encyclopedia of Chemical Technology, V17, p1, 1996]. The whole size of  $\beta$ -cyclodextrin is not sufficient large for  $\beta$ -cyclodextrin particles to stay between fiber molecules and to improve fiber properties. Its unique cavity configuration is the nature of  $\beta$ -cyclodextrin. without the existence of stabilizer material.

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### DISCLOSURE OF THE INVENTION

This invention provides methods to impart new functions and to improve existing properties of treated natural and man-made fiber textile materials with the application of nano-particle covalently coupled onto fiber molecules. Also, this invention provides a variety of nano-particle materials, with potential cavity configuration, generated and formed by the methods disclosed herein. In particular, this invention provides methods and materials to impart properties, such as, odor-control, soil release, better abrasion resistance, better performance and hand, and adding weight, to treated natural and man-made fiber textile materials.

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In one embodiment, provided is a method to apply nano-particles, all three dimensions of these nano-particles range from 1 nm to 100 nm into natural and man-made fiber textile materials to improve their performs. The nano-particles in this range can penetrate into the natural fibers. On the other hand, nano-particles in this range will create space hindrance between the fiber molecules. Space hindrance of this size between fiber molecules will play the functions of improving molecular movement over each other during fiber deformation. For cellulose fibers, nano-particles in this range will break some of the intrinsic hydrogen bonds between the fiber molecules also. Then, the properties of wrinkle-resistance and crease-retention are imparted to the cellulosic fibers. Star compounds, dendritic polymers, hydrophilic-hydrophobic block copolymers, or clathrate compounds, i.e. starch, linear or branched, includes amylose, dextrin and syrup, with or without nonpolar molecules or nonpolar segments of compound, etc., are such kind of nano-particle materials.

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In one embodiment, provided is a method to apply nano-particles with unique nano-helix configuration with potential nano-cavity of the hydrophilic outer wall and hydrophobic inner wall on natural and man-made fiber textile materials to have new functions. Such nano-cavity

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can trap and enclose various kinds of compound to possess numerous functions. For example, with the capabilities of trapping and enclosing odor materials and non-polar poison gas, the function of odor-control and gas absorption to the natural and man-made fiber textile materials can be imparted; nano-particles enclosing anti-microbial drugs and/or perfumes can add the function of slow-release of drug and fragrance to the textile materials; nano-particles enclosing hydrophobic material can add water-repellent functions to the textile materials; nano-particles enclosing oil-proof material can add oil-repellent function to the natural and man-made fiber textile materials. And nano-particles enclose the materials having other desired characteristics could add desired functions to the natural and man-made fiber textile materials. Starch, including amylose, dextrin and syrup are such kind of materials. Methods are provided to add one or more functions to the natural and man-made fiber textile materials in chemical treatment.

In one embodiment, provided is a method to generate and to form nano-helix particles with hydrophobic and non-polar molecule or non-polar segments compounds. These stabilizer compounds play the role of stabilizing helix configuration of nano-particles as well. Paraffin, hydrocarbon, halohydrocarbon, polyethylene, ethylene glycol and its derivatives, polyethylene glycol, non-polar parts of organic amine, organic amid, silicones, stearic acid, sodium olefin sulfonate and surfactant etc. are such kind of compounds. The selection of stabilizer compounds depends on the whole process and treatment solution composition as described herein.

In one embodiment, provided is a method to have covalent bonds to keep nano-helix configuration of nano-particle and to couple nano-particles onto fiber molecules inside the fiber structure.

#### MODES FOR CARRYING OUT THE INVENTION

Methods and materials are provided. Using these methods and materials disclosed herein, properties such as odor-control, soil release, better abrasion-resistance, better performance and hand, and adding weight, etc. can be imparted to natural and man-made fiber textile materials.

Nano-particles are generated and formed herein from star compounds, dendritic polymers, hydrophilic-hydrophobic block copolymers, or clathrate compounds. In particular, methods are

provided to generate and to form nano-particles from starches, linear or branched, preferably amylose, syrup and dextrin, with the molecule weight in the range of 1,000 to 1,000,000, preferably 1,000 to 15,000, with hydrophobic and non-polar molecule or non-polar segment compounds. These nano-particles have nano-helix configuration with hydrophilic outer and hydrophobic inner walls, respectively. The sizes of the nano-helix are around 1.5 nm in diameter; 2 - 10 nm, even longer in length, depends on the helix stabilizer compound. This length of helix complex (with stabilizer) can be determined with small angle X-ray scattering.

Covalent bond is created to couple nano-particles within fiber structure. The materials for coupling are: epichlorohydrin, polycarboxyl acid or other formaldehyde-free coupling agents; DMDHEU (dimethyloldihydroxyethylurea) or other similar urea compounds; periodate and urea or sulfite and other systems correspond to different functional groups of different nano-particles. Some of the man-made fiber, i.e. polyester fiber, has not the conventional reactive groups and can not swell in aqueous solution. Binding materials (i. e. self-crosslinking acrylic polymer, etc.) are adopted to bind nano-particle and coupling agent onto such fibers.

In solution, not only amylose can, dextrin, syrup, even some kinds of branched starch can also form the helix and/or interrupted helix configuration in a suitable condition [W. Banks, Starch and its Components, John Wiley and Sons, Inc. 1975, p67-77]. The outer and inner walls of the helix are discovered to be hydrophilic and hydrophobic, respectively. Stabilizer of hydrophobic and non-polar molecule or non-polar segment compounds will help the formation and the stabilization of the nano-helix configuration. Nano-helices of starch (including amylose, dextrin and syrup) can penetrate into natural fibers. The nano-helix configuration will be further held with the covalent bonds to fiber molecules and fixed by the covalent bonds between the hydroxyl groups on the helices. After coupling with fiber molecules, the nano-helix can add numerous functions to the natural and cellulosic fibers. The properties of the enclosed compounds will then determine the new functions imparted onto treated materials. For the purposes of multi-functional treatment, several different compounds can be wrapped in the cavities of nano-helices respectively. Applying such mixed solution of starch nano-helices will then add multiple functions onto the natural and man-made fiber textile materials. Starch nano-helices particles that coupled on fiber molecules will impart the natural and man-made fiber

textile materials with odor and gas absorption, wrinkle-resistance, crease-retention, soil-release, better mechanical properties and other features:

- a. Having the cavities totally or partially empty after coupled or bound on the fibers with the removal the stabilize compound, the function of deodorant and gas absorption can be added to the natural and man-made fiber textile materials.
- b. Enclosing partial molecule of silicones inside the cavities, the function of water repellent can be added to the textile materials.
- c. Enclosing partial molecule of fluorohydrocarbon inside the cavities, the function of oil-repellent and soil-release can be added to the natural and man-made fiber textile materials.
- d. Enclosing organic amine type drugs to possess slow release of anti-fungal and anti-microbial functions.
- e. The penetration and bonding of starch helix conduct wrinkle-resistance, crease-retention, and better strength and abrasion-resistance.

### INDUSTRIAL APPLICABILITY

More than 100 formulas for various functions of chemical treatments can be formed. For simplification, we only list a little more than 30 formulas (see Table II) for demonstration.

The process comprises several steps. It concludes preparing treatment solution, adding the solution to natural and man-made fiber textile materials and drying and curing the textile materials.

A typical treatment solution comprises: Starch, 1 - 15% owb; Coupling agents, 2 - 20% owb; Softeners, suitable amount; Surfactants, suitable amount; Catalysts, suitable amount; Helix stabilizer, 0 - 5% owb non-polar molecules or compounds with non-polar segments, i.e., ethylene glycol diethyl ether, ethylene glycol derivatives or polymers, polyethylene, hydrocarbon, fluorohydrocarbon, silicones, amine, various surfactants and others, such as UV absorbents anti-fungal and anti-microbial, suitable amount. For more functions, economy, safety etc. numerous different stabilizer combination could be introduced.

Examples of raw materials mainly are listed in the Table I.

Table I, Raw Materials Examples

Symbol	Raw Materials
SD	Starch (MW 1,000 – 15,000)
2D	DMDHEU(low aldehyde)
Cat	Catalyst $MgCl_2$
FA	Flurohydrocarbon
Dg1	N-dodecyl guanidine sulfate or Terbinafine hydrogen chloride
Dg2	Other drug
FR1	Bromo olefin amine hydrogen chloride
UVP1	2-(2'-hydroxy phenyl) benzotriazole
UVP2	2-hydroxybenzo phenones
PI	Polycarboxyl
UR	Urea
ECH	Epichlorohydrin
EE	Ethylene glycol diethyl ether
SL1	Amino functional silicone
SL2	Dimethyl silane

More than 30 examples, their formulas and applications are listed in Table II. Obviously, almost every textile process parameter change, different seasons, different end uses would have the reason to adjust the formulas. Table II listed the composition of the aqueous treatment solution.



Table II, Examples, Their Formulas\*\* and Applications

		Raw Materials											Functions*											Applications	
		SD	2D	Cat	ECH	PI	UR	EE	SLI	SL2	FA	Dg1	Dg2	FRI	UVPI	UVP2	WR	DP	DS	DO	WP	OP	SR		MP
1	A	10	12	2.5				0.	2								✓	✓		✓			✓	✓	Outwear
	B	10			2.5				2																
	C	10					0.2	1.7	1	2															
2	A	12	18	4.5				1.3	2	10							✓	✓		✓			✓	✓	Water-repellent
	B	12			4.0				2	10															
	C	12				0.2	2.6		2	10															
3	A	12	18	4.5				1.3		5	10						✓	✓		✓			✓	✓	Water-repellent Oil-repellent Soil-Release
	B	12			4.0					5	10														
	C	12				0.2	2.6			5	10														
4	A	9	16	4				1				2					✓	✓		✓			✓	✓	Cotton Socks
	B	9			2.5							2													
	C	9				0.2	1.7					2													
5	A	7.5	10	2.5				1.	2			2					✓	✓		✓			✓	✓	Underwear
	B	7.5			2.5				2			2													
	C	7.5				0.2	2.2		2			2													
6	A	12	18	4.5				1.3	2	5	10		30				✓	✓		✓			✓	✓	Decorate Fabric Carpet
	B	12			4.0				2	5	10		30												
	C	12				0.2	2.6		2	5	10		30												
7	A	9	16	4				1									✓	✓		✓			✓	✓	Protect Cloth
	B	9			4.0																				
	C	9				0.2	1.7																		
8	A	12	18	4.5				1.3		5	10						✓	✓		✓			✓	✓	Military Use
	B	12			4.0					5	10														
	C	12				0.2	2.6			5	10														
9	A	12	18	4.5				1.3	2				30	5	5			✓					✓	✓	Summer Wear & Ramie
	B	12			4.0				2				30	5	5		✓	✓							
	C	12				0.2	2.6		2				30	5	5										
10	A	12	18	4.5				1.3									✓	✓		✓			✓	✓	Wool, Silk
	B	12			4.0																				
	C	12				0.2	2.6																		
11	A	12	18	4.5				1.3					20				✓	✓		✓			✓	✓	Medical textiles
	B	12			4.0								20												
	C	12				0.2	2.6						20												

Functions\*: WR – Wrinkle-Resistance;  
 DP – Durable Press (Crease Retention);  
 DS – Drug-Slow-Release;  
 DO – deodorant;  
 WP – Water-Repellency;  
 OP – Oil-Repellency;  
 SR – Soil-Release;  
 MP – Enhance Mechanical properties (Strength & Abrasion Resistance).

\*\* All the data mean absolute weight (grams) for 100 grams of fiber, and they should be adjusted to fit the real needs.

### Examples:

#### Example 1, Twill Cotton Fabric:

a. Solution: (% of product as received based on bath weight)

	A	B
Starch	10	0
DMDHEU (Buffered, Unmodified)	12	12
Softeners	3 – 6	3 - 6
$(C_2H_5O)_5C_2H_5OCOC_{11}H_{23}$	1	0
Surfactants	0.1	0.1
$MgCl_2 \cdot 6H_2O$ (64%)	3	3

b. Pad, Wet Pickup 65% - 70%

c. Drying and Curing Conditions: appropriate for resin and equipment.

#### Test Results:

	A	B
Durable Press (AATCC 124)	3.0	3.3
Tensile, Fill (ASTM D5034), (lb.)	76.04	57.76
Ratio of Tensile, Fill	1.32	1.00

Flex, Warp (ASTM D3885), (cycles to failure)	656	379
Ratio of Flex, Warp	1.73	1.00
% Shrinkage, Warp (AATCC 135)	-2.9	-2.5
% Shrinkage, Fill (AATCC 135)	-0.2	-0.1
Odor after absorbed (35 mg./3 g cotton)	Weak or nil	strong
Free Formaldehyde (AATCC 112-1998)	418	658
Ratio of Free Formaldehyde	0.64	1.00

### Example 2, Sheeting Cotton Fabric

a. Solution: (% of product as received based on bath weight)

	C	D
Starch	7.5	0
DMDHEU (Buffered, Unmodified)	10	10
Softeners	3 - 6	3 - 6
$(C_2H_5O)_5C_2H_5OCOC_{11}H_{23}$	1	0
Surfactants	0.1	0.1
$MgCl_2 \cdot 6H_2O$ (64%)	2.5	2.5

b. Pad, Wet Pickup 65% - 70%

5 c. Drying and Curing Conditions: appropriate for resin and equipment.

### Test Results:

	C	D
Durable Press (AATCC 124)	3.0	3.1
Tensile, Fill (ASTM D5034), (lb.)	80.87	68.13
Ratio of Tensile, Fill	1.19	1.00
Flex, Warp (ASTM D3885), (cycles to failure)	1751	990
Ratio of Flex, Warp	1.77	1.00
% Shrinkage, Warp (AATCC 135)	-1.3	-1.3
% Shrinkage, Fill (AATCC 135)	-0.6	-0.6
Odor after absorbed (35 mg./3 g cotton)	Weak or nil	Strong

Free Formaldehyde (AATCC 112-1998)	437	521
Ratio of Free Formaldehyde	0.84	1.00

### Example 3, 100% Polyester Fabric

The composition of treatment solution is the 1/3 quantity of that of example 2, but add 5% self-crosslinking acrylic polymer, Rhoplex K-3 (Rohm & Hssa Inc). The treatment imparts the fabric with deodor, better hand and moisture regain.

### The Method to Evaluate the Odor-Control

Use the odor of dried garlic powder to simulate the unpleasant odor, i.e. oil odor from kitchen work, or human body (axillary) malodor, etc.

The samples evaluated are treated fabrics with above formulas for comparisons.

Put 35 mg of dried garlic powder (distributed by Aldi, Inc. Batavia, IL 60510 USA) into the bottom of a glass bottle with a volume around 120 cc. Put in 3 grams of fabric sample, which is cut to be 15 mm wide stripe Seal this bottle by a tight cover for 1 hour.

Open the covers of different bottles for the comparison of the intensity of garlic odor.

### CONCLUSION

Methods are provided with the application of nano-particles to impart treated natural and man-made fiber textile materials with excellent odor-control, soil release functions, better abrasion resistance, better performance, better hand and adding weight, and, in the case of the cellulosic fiber materials, with good wrinkle resistance, but lower the reduction in tensile strength. Methods are provided also to generate, to form and to stabilize the nano-helix particle with hydrophobic and non-polar molecule or non-polar segments compounds. Methods are provided to open new doors for more potential functions based on its nano-cavity structure.

We claim

1. The method of modifying the natural and man-made fiber textile materials, wherein the nano-particles with all their three dimensions ranging from 1 to 100 nm, are coupled on the fiber molecules with covalent bonds, or bound on fiber to impart numerous functions.
2. The method of claim 1, wherein the nano-particles comprise dendritic compounds, star compounds, hydrophilic-hydrophobic block copolymers, inorganic particles or clathrate compounds.
3. The method of claim 2, wherein the clathrate compound comprises starch, linear or branched, which includes amylose, dextrin and syrup, with helix stabilizer.
4. The method of claim 3, wherein said stabilizer comprises non-polar molecules or non-polar segments of compound, etc., helping starch to form and stabilize more perfect helix structure.
5. The method of claim 3, wherein the starch forming the helical clathrate, is with the molecular weight ranging from 1,000 to 1,000,000, preferably 1,000 to 15,000.
6. The method of claim 3, wherein starch molecule clathrates non-polar molecule to form helical structure, said such non-polar molecules comprise ethylene glycol and its derivatives and polymers, polyolefin, hydrocarbon, polyolefin oxide, iodine etc.
7. The method of claim 3, wherein the starch molecule clathrates non-polar segments of compounds to form helical structure. said such compounds comprise anionic, cationic or nonionic surfactants, stearic or oleic acid and their esters or salts, organic acids and their esters or salts, amines, amides etc.
8. The method of claim 3, wherein the starch molecule can form partial helical conformation without non-polar molecule of non-polar segment of compound.

9. The method of claim 3, wherein the starch clathrate has nano-cavity with non-polar inner wall and polar outer wall.

10. The method of claim 1, wherein binding compounds or polymers are adopted for nano-particles bound on fiber, i.e. self-crosslinking acrylic polymers etc.

11. The method of claim 1, wherein said numerous functions comprise several or all the following properties, such as odor-control, soil release, better abrasion resistance, better performance, better hand and adding-weight.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/10951

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : D06Q 1/02; D06M 13/00

US CL : 8/115.51, 115.6, 116.1; 19/145

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/115.51, 115.6, 116.1; 19/145

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EAST/USPAT, JPO, EPO, US-PG-PUB, DERWENT;

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,589,256 A (HANSEN et al) 31 December 1996, entire document.	1-11
A	US 5,693,411 A (HANSEN et al) 2 December 1997, entire document.	1-11
A	US 5,543,215 A (HANSEN et al) 6 August 1996, entire document.	1-11

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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